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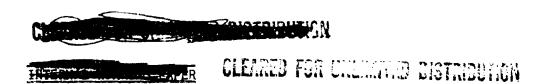
BIOLOGICAL CORROSION AT NAVAL SHORE FACILITIES

(WITH APPENDED BIBLIOGRAPHY ON BIOLOGICAL CORROSION)

Ву

Harold P. Vind, Ph. D., and Mary Jane Noonan

20 July 1966



U. S. NAVAL CIVIL ENGINEERING LABORATORY Port Hueneme, California



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TN-831

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by

Harold P. Vind, Ph. D., and Mary Jane Noonan

ABSTRACT

Each year the Navy spends millions of dollars for the maintenance, repair, and replacement of structures and utilities damaged by corrosion. Expenditures resulting from the corrosion of steel waterfront structures in the regions of periodic wetting by sea water are especially great.

Considerable evidence indicates that bacteria and other organisms frequently initiate or accelerate corrosion of metals. Microorganisms accelerate corrosion by producing hydrogen sulfide or acids, both of which are highly corrosive to iron and steel. Thiobacillus thioxidans, the bacteria which convert sulfides or free sulfur to sulfuric acid, may cause the extremely rapid corrosion of steel waterfront structures in the intertidal zone; but this has not been established by experimental evidence

Experiments were undertaken at the U. S. Naval Civil Engineering
Laboratory to ascertain if the presence of microorganisms is necessary
for corrosion to occur. It was shown that, in aerated sea water, iron
corrodes fairly rapidly whether or not microorganisms are present; but
that, in sea water from which oxygen is excluded, iron rusts very slowly
unless sulfate-reducing bacteria or their metabolic by-product, hydrogen sulfide, is present. To induce rapid anaerobic corrosion, the bacteria
must be supplied with carbohydrates or other nutrients. Anaerobic conditions and bacterial nutrients might both be found in the layer of slime
that accumulates on the surfaces of structures placed in the ocean.

Another experimental finding at the U. S. Naval Civil Engineering Laboratory was that the carbonic anhydrase inhibitor, acetazolamide, is an effective inhibitor of sea water corrosion.

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INTRODUCTION AND STATEMENT OF PROBLEM

Annually the Navy spends millions of dollars for the maintenance, repair, and replacement of structures and utilities damaged by corrosion. An understanding of the causes of corrosion and means of preventing corrosion is thus of paramount concern to the Naval Facilities Engineering Command. Considerable evidence indicates that bacteria and other organisms frequently initiate or accelerate corrosion. A paramount question is whether organisms play a major or an insignificant role in the corrosion of structures maintained by the Naval Facilities Engineering Command.

CORROSION PROBLEMS AT NAVAL SHORE FACILITIES

The extent and severity of corrosion of structures at Naval Shore Activities vary with the location of the structures. Metal structures that are buried, situated above ground, or located on a waterfront each exhibit unique patterns of corrosion and each requires different maintenance and corrosion prevention measures. Some of the corrosion problems have been satisfactorily controlled but others remain unsolved.

Corrosion of Underground Structures

Corrosion of Underground structures or utilities continue to impose a serious maintenance problem at some Naval activities. Steam condensate return lines and heat distribution systems located below the water table constitute a major problem, though corrosion of all buried structures is rapidly being reduced by better drainage in the soil, by cathodic protection, and by the use of substitute materials such as epoxy-glass and polyvinyl chloride.

Experiences in the Gulf Naval Division illustrate the effectiveness of cathodic protection in the prevention of underground corrosion. In 1953, several buried fuel tanks in that division were found to be severely corroded even though the exteriors of the tanks had been covered with an asphaltic paint prior to installation. In 1953 and 1954, cathodic protection equipment of the impressed voltage type was installed on all of the buried fuel and water tanks in the division at an installation cost of approximately one to ten percent of the cost of the tanks. Measurements made in 1964 indicate that very little

corrosion has occurred since the cathodic protection equipment was installed. Buried fuel and water lines in the Gulf Naval Division have a fur history and, prior to 1955, frequent replacement of repair of buried pipes was necessary. At the Dallas Naval Station, for example, the monthly cost of repairing buried fuel and water lines was in excess of one thousand dollars. In 1955, cathodic protection equipment of the impressed voltage type was installed on all buried pipes, and the need for repair since has been negligible.

Comparable success in prevention of underground corrosion has been achieved through the use of plastic pipe and the construction of concrete drainage trenches. Thus, although bacteria may play a significant role in the corrosion of underground structures and utilities, their depredatory activities can be controlled.

Corrosion of Above Ground Structures

Since the corrosion of metal structures above ground cannot be arrested by cathodic protection, corrugated steel shops, warehouses, coal bunkers, and similar structures still present some maintenance problems (Figure 1). Painting is the sole effective maintenance procedure for protecting such buildings or structures. Primers that prolong the life of overcoated paint films applied to metal have been developed; yet, for various reasons, the paint still fails. In many instances, rusting of the underlying metal appears to precede the peeling of the paint, and, to date the importance of bacteria in this sequence of events is not known. Frequently, corrosion of corrugated steel structures occurs where wood contacts metal, a problem especially severe in tropical climates. Wood-rot*ing fungi that produce organic acids might be causative agests, but this too has not yet been established. Compared to the problems faced in the maintenance of buried iron pipes and steel waterfront structures, those faced in the maintenance of metal buildings above ground are relatively minor.

Corrosion of Waterfront Structures

The most serious corrosion problems at Naval activities occur on the waterfront. In every Naval Division, at least one major waterfront structure is failing or has recently failed and been replaced as a consequence of the corrosion of structural steel. Typically, the structures involved are fifteen to twenty years old-

As yet, measures preventing correction of steel waterfront structures have not been as successful as are those used with buried tanks and pipes. Cathered stotection does not prevent corresion of

portions of steel structures extending above or suspended above the water line, the region of most severe corrosion, and, even though effective, cathodic protection is not widely used to prevent the corrosion of the submerged portions of steel waterfront structures. Likewise, the use of protective coatings to prevent the corrosion of waterfront structures has met with but limited success.

Corrosion of steel bulkheads, underdeck piping, and other waterfront structures, such as electric light poles (Figure 2), is rapid at most harbors, although exceptions exist. At Quonset Point, Rhode Island, for example, a steel bulkhead less than twenty years old is failing; whereas across the bay at Newport, Rhode Island, a steel bulkhead forty years old remains in good condition. Even an experimental concrete jacket failed to halt the corrosion at Quonset Point. One explanation for the differences in service life of the bulkheads in the two harbors is the degree of pollution of the water. At Quonset Point, the harbor water is said to be highly polluted; whereas, at Newport, tidal action brings clean water of the deep offshore channel to the harbor. Another possible cause for the differences cited is that on several occasions, oil has been accidentally spilled near the bulkhead in the Newport Harbor, thereby coating the bulkhead with a thin film of oil. (The age-old household method to prevent rusting by a periodic application of a thin coat of oil might save the Navy considerable sums.)

A twenty-year old bulkhead or sea wall several miles long at the Naval Air Station, Floyd Bennet Field, New York, is in an advanced stage of deterioration. For several hours before and after low tide, most of the structure is completely dry. A large section, shown in Figure 3, is so badly perforated in the mean low tide zone that it no longer retains the earthen fill. Other sections, such as that shown in Figure 4, still retain the earthen fill, but they are in need of extensive repair.

During World War I, an extensive wood-piling bulkhead was constructed at the U.S. Naval Base, Norfolk, Virginia. During World War II, the base was modernized and concrete-decked sheet steel bulkhead; were installed. The sheet steel piling was driven a short distance in front of the old wooden bulkhead (which was not removed) and an earthen fill was placed between. By 195t it was already apparent that the new bulkhead was rapidly deteriorating (Figure 5). By 1959, the steel bulkhead was perforated at many spots (Figure 6) and large sections of the steel wale had fallen off. In late 1959, during Burricane Dönna, the steel bulkhead collapsed and released the fill between the old and the new bulkhead collapsed and released the fill between the old and the new bulkheads. Fortunately, the older wooden bulkhead remained intact and prevented hore serious damage. The two bulkheads have since been faced with a third bulkhead of concrete and steel. Should that fail also, the old wooden bulkhead, remaining intact a few feet rehind, will again serve its intended function.

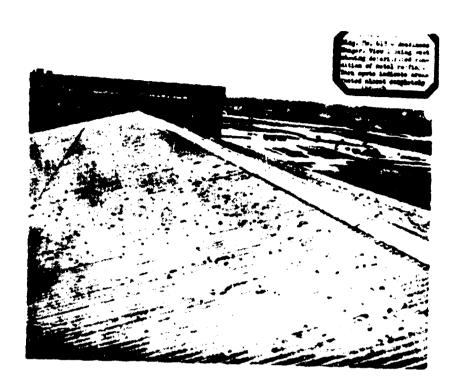


Figure 1. Metal roof perforated by corrosion.
(Naval Station, Newfoundland, 1962)



Figure 2. Metal light pole exposed to ocean spray. (Naval Shipyard, Norfolk, 1958)



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Figure 3. Loss of earthen fill by damaged bulkhead. (Naval Air Station, New York, 1963)



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Figure 4. Corroding bulkhead in need of repair.
(Naval Air Station, New York, 1963)

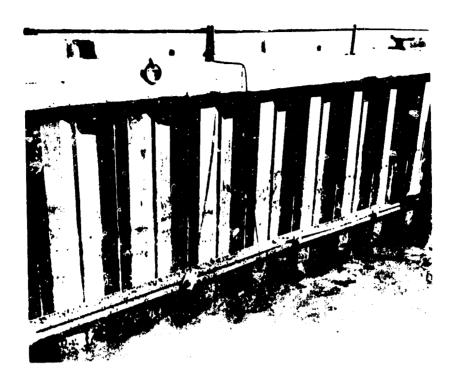


Figure 5. Bulkhead 3 years before hurricane Donna. (Naval Air Station, Norfolk, 1956)

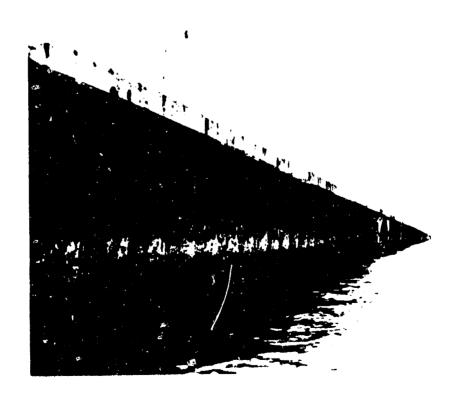


Figure 6. Bulkhead immediately prior to hurricane. (Naval Air Station, Norfolk, 1959)

In recent years, steel H-piles have replaced wooden piles in the piers and wharves at Naval Activities on the Gulf Coast. The piles corrode even though they are heavily covered with a bitumastic coat ing before they are driven. Corrosion occurs primarily at, or just above, the water line and occasionally at, or just above, the mud line. Various aplash zone coatings have been employed to prevent this corrosion; but at the breaks or cracks that eventually develop in the coatings, corrosion occurs more rapidly than if there were no coatings. Steel piles of the Galveston pier are now being encased in concrete that extends several feet below the water line, though it is not at all certain that the concrete caps will prevent further corrosion. Similar caps did not prevent corrosion of steel piles at Quonset Point, Rhode Island, nor at the Boston Naval Shipyard. Whether the steel piles of the piers at the various gulf ports will last sufficiently longer than wooden piles to justify their higher cost remains to be seen.

Typical of the larger steel waterfront structures to succumb to corrosion are two breakwaters at Corpus Christi, Texas. The breakwaters (Figures 7 and 8), constructed of huge steel cylinders, and decked with concrete are but fifteen years old and are at present riddled with holes at the water line. One will be abandoned and the other will, if possible, be repaired.

Corrosion of Mid Ocean and Undersea Structures

Presently, Naval Facilities Engineering Command (NAVFAC) is primarily engaged with the design, construction and maintenance of structures on the shore of the oceans. In the future, NAVFAC may assume a primary responsibility for the design, construction, and maintenance of floating bases in mid-ocean and underwater bases or structures both on the continental shelves and in the deep ocean. NAVFAC activities can anticipate corrosion problems in these new environments.

ORGANISMS THAT INFLUENCE THE CORROSION OF METALS

It is well established that the immediate chemical reaction called corrosion is an electrochemical reaction rather than biochemical. Microorganisms, however, release chemicals into the immediate environment of the iron, or remove them from this environment thereby causing changes in the corrosion rate. The discharge of metabolic by-products of bacteria can even cause rapid and severe corrosion to occur in an environment where corrosion would otherwise not occur at a significant rate. Because of the economic importance of corrosion to the Navy, it is well to review the ways in which various organisms are reputed to influence corrosion rates.

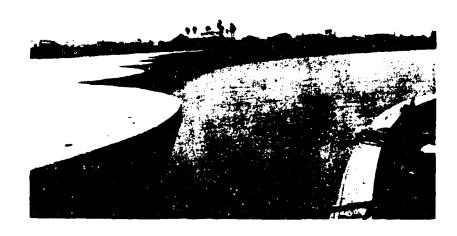


Figure 7. Concrete decked steel breakwater.
(Naval Air Station, Corpus Christi, 1959)

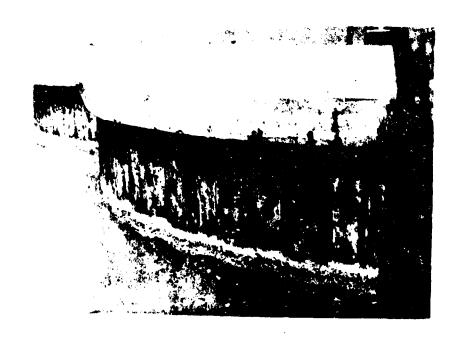


Figure 8. Corrosion of sheet piling on breakwater. (Naval Air Station, Corpus Christi, 1959)

Organisms That Produce Hydrogen Sulfide

Hydrogen sulfide significantly accelerates the corrosion of iron, but it is volatile and somewhat unstable and does not remain long in natural waters unless produced continuously. Hence, sulfide corrosion can be attributed to the agent or processes producing hydrogen sulfide.

. 0

Some of the hydrogen sulfide found in sewage or heavily polluted waters arises from protein decomposition, but most of the hydrogen sulfide occurring in natural waters is attributable to reduction of sulfate ions by bacteria. Sulfate ions occur widely in ground and river waters, and about ten percent of the salt in sea water consists of sulfates. Bacteria capable of reducing sulfates to sulfides are widely distributed both in terrestrial and marine environments and, whenever conditions are appropriate, the bacteria produce copious quantities of hydrogen sulfide.

Most microorganisms reduce traces of sulfate sulfur to sulfhydryl or disulfhydryl sulfur when they synthesize proteins. A few highly specialized bacteria can utilize sulfate ions as hydrogen acceptors in their energy producing reactions. These truly sulfate-reducing bacteria are generally classed as a single genus, but their classification is still uncertain and their nomenclature is confusing. Various names have been given to sulfate-reducing bacteria; names such as Spirillum desulfuricans, Desulforistella hydrocarbonastica, Vibrio desulfuricans, and Desul, ovibrio aestuarii. Confusion regarding the nomenclature of sulfate-reducing bacteria, which should likely all have the same genus name, arišes from the difficulty in isolating pure cultures of these organisms and from the fact that supposedly different species are interconvertible by gradual acclimatization.

Sulfate-reducing bacteria require special conditions for growth. They are in general obligate anaerobes and will thus usually grow only in the complete absence of molecular oxygen. Growth of sulfate-reducing bacteria is often initiated in the thin film of bacterial slime that forms on iron surfaces exposed in the ocean or buried in wet seil. As rusting continues, the oxygen within the bacterial slime is depleted by oxidation of the iron, thus initiating anaerobic conditions that promote growth of obligately anaerobic bacteria. Aerobic bacteria within the slime will also utilize oxygen thus creating anaerobic conditions. Once growth of sulfate-reducing bacteria begins, there is a tendency for the anaerobic region to spread because hydrogen sulfide, itself an active reducing agent, is produced.

Sulfate-reducing bacteria cannot obtain energy for their growth and activity by reducing sulfate sulfur to sulfhydryl sulfur and, in fact, they must supply considerable energy to effect the reduction. The bacteria are able, however, to more than regain this energy by oxidizing hydrogen or carbon with the oxygen released from the sulfate ions from which the sulfur atoms have been extracted. Thus sulfate-reducing bacteria not only require sulfate ions and anaerobic conditions, but a supply of food or "fuel." They are not fastidious in their food requirements and can oxidize a variety of organic substances as well as molecular hydrogen.

Organisms That Metabolize Cathodic Hydrogen

Theoretically, hydrogen is produced at cathodic sites on corroding metal and the removal of hydrogen from these sites is believed to be one of the principal rate regulating steps in the corrosion process. The belief that sulfate-reducing bacteria accelerate anaerobic corrosion by metabolizing the cathodic hydrogen is substantiated by evidence that sulfate-reducing bacteria readily metabolize molecular hydrogen.

The hydrogen acceptor in aerobic corrosion is molecular oxygen, but in anaerobic sulfide-corrosion sulfate ions are presumed to be the hydrogen acceptors. Although sulfate ions are not ordinarily capable of serving as hydrogen acceptors, it is believed that sulfate-reducing bacteria enable them to function in this capacity. It has also been suggested that methane-producing bacteria, as well as nitrate-reducing bacteria, might enable carbon dioxide molecules or nitrate ions to function as acceptors for cathodic hydrogen from corroding metal.

Hydrogen gas is slowly liberated from the surface of iron filings⁵ kept in contact with a deaerated aqueous solution of inorganic salts buffered to a pH of 6.0 - 6.5. The pH of the solution gradually rises to about 8.0 at which point the reaction slows down considerably. The hydrogen so liberated may be collected if the reaction is carried out in an inverted U-necked cylinder originally filled to capacity with the solution. As it coilects, the hydrogen forces some of the solution from the mouth of the cylinder. Sulfate-reducing bacteria can then be cultivated in the cylinder, providing the solution in the cylinder contains sulfates and carbonates or bicarbonates. No energy-yielding substrate other than the hydrogen liberated by the corroding metal is required.

Growth of sulfate reducing bacteria under the conditions cited above and the subsequent production of hydrogen sulfide are held as proof that the bacteria repolarize cathodic sites on corroding metal,

i.e., that they scavenge the thin film of nascent hydrogen adsorbed to the surface of the metal and presumed to govern its corrosion. It would seem, however, that the activity of the bacteria under the conditions cited might merely demonstrate that sulfate-reducing bacteria can utilize molecular hydrogen spontaneously liberated from corroding metal.

Whether removal of cathodic hydrogen is the role played by sulfate-reducing bacteria in the corrosion of iron is not merely an academic question. If this is their role, sulfate-reducing bacteria engaged in the production of hydrogen sulfide via the metabolism of substrates other than cathodic hydrogen would have no influence on corrosion rates; and anaerobic bacterial corrosion would proceed as rapidly in the absence as in the presence of other energy sources. Elucidation of the mechanism has, therefore, practical significance. A basic question is whether the process of hydrogen sulfide formation is itself the process accelerating corrosion, or whether the liberated hydrogen sulfide reacts with iron to accelerate its corrosion. Of course it is possible that both of the processes accelerate corrosion.

Organisms That Oxidize Sulfur to Sulfuric Acid

Hydrogen sulfide produced in an aqueous environment escapes at the surface of the liquid where it may be subsequently adsorbed onto the surfaces of structures existing in the vicinity. Some of the hydrogen sulfide reacts with air to form free sulfur, which also may be adsorbed on nearby structures. The adsorption of sulfides and free sulfur frequently occurs on the walls of sewage conduits and sewage tanks and might occur at or just above the water line on the surfaces of waterfront structures.

In an aerobic aqueous environment, sulfides and free sulfur are rapidly converted to sulfuric acid by the bacterium, <u>Thiobacillus</u>, of which the best known representative is <u>Thiobacillus thiooxidans</u>. This species is known to produce sulfuric acid with concentrations as high as ten percent. When the acid is produced on the surfaces of metal tanks or metal sewage conduits, it accelerates their corrosion significantly. This type of corrosion is also frequently responsible for severe damage to crude-oil storage tanks and pipe lines. Acid corrosion induced by <u>Thiobacillus thiooxidans</u> is, under certain conditions, the most serious type of corrosion encountered.

It is a distinct possibility that the rapid and severe corrosion that usually occurs on steel waterfront structures in the region of periodic westing is also caused by the localized production of sulfuric acid by <u>miobacillus thioxidans</u>. This has not been substantiated,

however, and, until further investigation is pursued, one can but merely speculate on the role played by sulfuric acid-producing bacteria on the deterioration of steel waterfront structures.

Organisms That Oxidize Ferrous Iron to Ferric Iron

Many bacteria are capable of oxidizing ferrous compounds, the initial products of corrosion, to ferric compounds. Some of the iron-oxidizing bacteria are strictly autotrophic and require no carbohydrate or other organic material for food. They obtain all of the energy required for their growth and activity by oxidizing ferrous ions and synthesize the necessary organic "building blocks" of cell components by "fixing" carbon dioxide. Some of the better known species of autotrophic iron-oxidizing bacteria are Thiobacillus ferrooxidans, Gallionella ferruginea, and Ferrobacillus ferrooxidans.

When iron rusts and resulting ferrous corrosion products are oxidized to ferric compounds, iron bacteria are usually found in great numbers. Many investigations have been made of the role played by the iron bacteria in the corrosion of iron; but that role, if any, is still rather obscure. The bacteria may accelerate the oxidation of the ferrous compounds, but again they may merely be capturing the energy of a chemical reaction that is but little influenced by their presence. Ferrous ions can be oxidized to the ferric state quite readily in the absence of any bacteria and, furthermore, the oxidation of ferrous iron to ferric iron does not necessarily have a significant influence on overall corrosion rates.

Many water supplies are rich in ferrous salts, especially ferrous carbonates, which are relatively soluble in water. Iron bacteria oxidize the ferrous salts to insoluble ferric hydroxides and under suitable conditions, cause large flocculent masses of characteristic reddish-brown ferric hydroxides and oxides to accumulate in such quantities as to clog the water mains. The source of the iron, however, usually is the water and not metal pipes.

Organisms That Produce Organic Acids

Most microorganisms produce a great variety of organic acids. Molds are especially capable of producing organic acids in quantities sufficiently great to markedly increase the acidity of their environment. Aspergillus niger, Penicilijum cyclopium, and numerous other species frequently attack the fabric of electrical insulation on power cables. Free acids accumulate on the surface of the exposed wire in sufficient concentrations to rapidly corrode the wire. This type of attack on electrical power lines, on coils of electric motors, and

other insulated electrical utilities and instruments is especially common in tropical areas. The organic acids produced by aerobic fungi also frequently cause the pitting and corrosion of aircraft fuel tanks and fuel storage tanks. 14

The organic acids liberated by microorganisms in a marine environment probably have but little influence on the corrosion of structures below the water line. The acids are not produced in sufficient quantities to alter the pH of sea water and there is no evidence that organic acids influence corrosion by any mechanisms other than by altering the pH. Organic acids liberated by microorganisms on the surfaces of steel structures extending above the water line might, however, accumulate in concentrations great enough to significantly increase the surface acidity. Under such circumstances the organic acids would speed up corrosion considerably. The microorganisms could not produce organic acids from the metal itself but they might produce the acids from organic fouling debris attached to the surface of the structure.

Organisms That Produce Oxygen

The presence of unicellular photosynthetic organisms in the ocean is well established and in sunlight many of them liberate oxygen, one of the principal agents accelerating corrosion. Where and how extensively diatoms and other photosynthetic organisms accumulate on the surfaces of iron and steel structures immersed in the ocean has received but scant attention. These organisms might well play an important role in the corrosion of metal structures in the splash and spray zones and in the intertidal zone.

Organisms That Form Films or Layers of Fouling Growth

In the thin film of bacteria, rust, and slime that readily accumulates on the surfaces of iron structures in the ocean, the concentration of dissolved gases differs considerably from that of the surrounding water. Both the bacteria in the film and the iron to which it is attached remove oxygen from the water faster than it can diffuse through the film; and consequently, conditions in the film are frequently anaerobic and ideally suited for the growth of hydrogen sulfide-forming bacteria. Anaerobic corrosion can, therefore, occur even in well-oxygenated areas of the ocean. Iron buoy chains, for example, are frequently covered with heavy black deposits having the tell-tale odor of hydrogen sulfide. Deep craters and grooves are found on the chains when the black deposits are removed. The adhering film of bacteria and slime can, however, serve to merely lower the concentration of oxygen, and not create anaerobic conditions. In such instances, the bacterial film probably retards corrosion significantly.

Larger fouling organisms such as barnacles and sea urchins also influence corrosion. and are especially active in destroying protective contings applied to metal to retard corrosion. Another mechanism whereby the larger fouling organisms influence corrosion is in the creation of so-called "oxygen concentration calls." The surface of the metal under a barnacle or other macrofouling organisms soon becomes anaerobic, whereas surrounding areas are exposed to more abundant supplies of oxygen. In consequence of the different oxygen concentrations, a galvanic concentration cell is formed and the electrical potentials set up in the metal induce corrosion and pitting to occur under the fouling organism. The effect is more to concentrate corrosion at localized areas than to increase the overall corrosion.

Fouling organisms have also been known to actively "bore" 18 into metal. For example, sea urchins may destroy steel piling. With their chisel-like "teeth," more commonly used to browse on sea weed, sea urchins continuously scrape the rust from the surface of steel piling leaving the bare metal ever exposed to the corroding action of sea water. Teredo and pholads have also been known to bore into lead sheaths of underwater cables. 19

To date, the important initial stage of fouling, the formation of a "primary film" 20 of dissolved organic material, bacteria, diatoms, algae and other marine microorganisms, has received but scant attention. The formation of the primary film is not only the first step in the process of fouling, but it is the first step in the process of bacterial corrosion of metals and in the bacterial decomposition of protective coatings. Attachment of microorganisms is also the primary step in terrestrial processes of biodeterioration. A better understanding of how microorganisms are attracted to and attached to surfaces is needed.

Recently performed studies have uncovered facts that alter long held concepts of the sequence of events in the fouling process. ZoBell, at Scripps Institute of Oceanography, has demonstrated that adsorption of dissolved organic matter to surfaces exposed in self water precedes the attachment of the bacteria. The bacteria utilize the adsorbed organic material as a source of nutrients and may be attracted by it. Preliminary results of studies underway at the Aerojet Corporation's Laboratory at Azusa, California reveal that pure cultures of marine bacteria do not readily adhere to surfaces exposed in sea water. A When algae grow in the water, however, bucteria and other micropromisms are readily attached to the surfaces.

Microorganisms do not morely reside on the suffaces upon which they accumulate, but are securely fastened to the surfaces and can be removed only by drastic cleaning methods. The composition of the comenting substance and the mechanism of adherence is not known.

That this substance is produced by algae or by the attaching mircoorganisms themselves is not known nor do we know that the substance is an attractant as well as an adhesive. Answers to these questions would likely provide clues for methods of preventing attachment of undesirable macro and microorganisms to surfaces of structures submerged in the ocean as well as surfaces of structures on land.

EXPERIMENTAL

Introduction

The study of biological corrosion was primarily confined to a "state of the art" search of the literature, but on a limited scale, laboratory experiments were also performed. One objective of the laboratory experiments was to determine relative rates of corrosion in a sterile environment and in an environment containing microorganisms. Another objective was to ascertain whether compounds of biochemical significance such as microbial metabolites, biological inhibitors, or biocidal agents influence corrosion rates. Because of their very great number, only a few such biochemicals were selected for laboratory investigation.

Methods and Materials

Measurement of Corrosion Rates. Corrosion rates were estimated by the simple procedure of determining the loss in weight of samples of iron after given exposures to a corrosive environment. The iron samples were weighed and then exposed to various corrosive environments for given periods of time. They were then freed of rust deposits, thoroughly cleaned, dried, and finally weighed again. The loss in weight was employed as a measure of the corrosion rate.

<u>iron Samples</u>. Analytical grade iron wire in 70 millimeter lengths was wound into coils of about one millimeter diameter. The coils were formed around a large hypodermic needle into the end of which the wires were inserted and held fast while the coils were wound. Each iron sample consisted of three of the small coils of wire. The initial weights of the sets of three coils ranged from about 190 to about 220 milligrams and were recorded to the nearest tenth of a milligram.

Inoculum. No attempt was made to employ pure cultures of microorganisms, because mixed cultures of microorganisms involved in the
corrosion of iron were desired. Scrapings and bits of soil surrounding
a heavily corroded buried pipe and flakes of rust from a steel bar
exposed in the harbor just above the water line, were mixed and

suspended in sea water containing glucose and beef extract. The resulting mixture was employed as the inoculum for the experiments performed in air. Scrapings from a block of wood removed from the harbor were added to the above described inoculum for the experiments in which influence of wood on the corrosion of metals was studied. Finally, scrapings from a submerged iron chain undergoing sulfide corrosion were added to the inoculum for the experiments performed under nitrogen or under a mixture of nitrogen and hydrogen sulfide. The latter inoculum was stored under a stream of nitrogen.

Gas Mixtures. Natural air was employed for the majority of the experiments. In those experiments requiring an oxygen-free atmosphere, water-pumped nitrogen gas was forced through the chambers in which the samples were stored. After the oxygen was flushed from the sample chamber, the flow of nitrogen was reduced to a rate of only a few milliliters per minute.

The mixtures of hydrogen sulfide and nitrogen employed for a few of the experiments were not of precise composition. A small hydrogen sulfide generator was placed in the nitrogen line. The generator contained numerous lumps of iron sulfide. A few milliliters of dilute hydrochloric acid were added daily (with the exception of weekends) and the hydrogen sulfide liberated was swept into the sample chamber by the incoming nitrogen. The flow of incoming nitrogen was sufficiently slow to preclude the sweeping away of all of the hydrogen sulfide in the sample chamber during a twenty-four-hour period.

The carbon dioxide-enriched air was produced in a similar manner. A carbon dioxide generator was inserted in the air line. The generator contained an excess of precipitated calcium carbonate and a few milliliters of dilute hydrochloric acid were added daily. Again, the flow of incoming air was sufficiently slow to preclude the sweeping away of all of the carbon dioxide from the sample chamber in a twenty-rour-hour period. The carbon dioxide-free air was produced by slowly bubbling the air through a potassium hydroxide solution.

Removal of Rust. In several preliminary experiments, as ultrassonic cleaning bath was employed to remove rust from the iron samples. The cleaning process was facilitated with carborundum powder. The loss in weight of control samples which had not been exposed to corrosion but which were exposed to the cleaning process was barely detectible.

The ultrasonic cleaning method alone proved inadequate for cleaning many of the iron wires hence, the majority of the samples were cleaned by brief exposure to dilute hydrochloric acid to which an inhibitor or "pickling" agent was added. The samples were further cleaned in the ultrasonic cleaning bath. The loss in weight of control samples cleaned by the combined acid and ultrasonic method was measurable but did not exceed about one-half percent of the original weight of the samples.

Control of pH. Unless otherwise noted, the initial pH of the various solutions in which the iron wires were exposed was adjusted to within a half pH unit of neutrality. No adjustments in the pH of the solutions were made during the experiments, however, as the majority of the solutions were maintained in flasks closed with cotton plugs. The pH of some of the solutions changed considerably during the experiment and variable pH was no doubt one cause for variation in corrosion rates within different flasks and from experiment to experiment.

<u>Sea Water</u>. The sea water employed in the various experiments was drawn from a deep well driven near the shore of the ocean. Chemical analysis indicated that the ocean was the source of the well water. For some of the experiments—a nutrient sea water was prepared by adding 1 gram of glucose and 0.5 gram of beef extract to one liter of sea water from the well.

General Procedure. The coils of iron wire in sets of three were placed in 50 milliliter Erlenmeyer flasks and covered with 20 milliliter portions of sea water or other aqueous mixtures. The flasks were then fitted with cotton plugs and sterilized in the autoclave under 15 pounds of pressure for one hour. (This treatment caused no detectible loss in weight of the iron wires.) When cool, the designated flasks were inoculated with a few drops of the appropriate mixture of nutrient sea water and natural rust deposits. The flasks were then stored in an incubator at 33°C for a stipulated period of time, usually three months. In the experiments in which gas mixtures other than a'r were utilized, the flasks were stored in large dessicator jars through which the gas mixture in question was forced to flow. The jars were partially immersed in a temperature-controlled water bath.

Experimental Results and Their Significance

The Influence of Oxygen on Corrosion. The iron wires corroded five to six times more rapidly in sterile sea water saturated with normal air than in sterile sea water saturated with oxygen-deficient air, i.e., with nitrogen (Table I). The true differences in aerobic

and anaerobic corrosion may be a little greater than indicated by Table I as there were several periods of several hours each at the beginning and end of the experiment when the anaerobic flasks were exposed to air. Furthermore, commercial nitrogen might contain traces of oxygen and small amounts of iron may have been removed with the rust when the samples were cleaned.

Table I. Influence of Mixed Wild Strains of Bacteria on the Corrosion of Iron Wire Immersed in Sea Water Cortaining No Added Nutrients

Percent Loss in Weight of Iron W	Vire it. Three	Months
Corrosion Environment	Bacteria Free	With Bacteria
Sea water saturated with air Sea water saturated with air	10.1% 12.5%	12-1% 6.3%
Sea water saturated with nitrogen Sea water saturated with nitrogen		1.9%

Ihe Influence of Bacteria on Corrosion. Bacteria had little or no influence on either the aerobic or anaerobic corrosion of iron wire immersed in sea water containing no added nutrients (Table I); but when they were supplied with a small amount of glucose and beef extract, bacteria had a great influence on anaerobic corrosion (Table II). In approximately three days the contents of the inoculated anaerobic flasks turned black and acquired the distinct odor of hydrogen sulfide. By the end of the experiment the combined loss in weight of the wires in the inoculated flasks was 6-1/2 times greater than the corresponding loss in weight of the wires in the sterile flasks.

Table II. Influence of Mixed Wild Strains of Bacteria on the Anaerobic Corrosion of Iron Wire Immersed in Nutrient Sea Water

Perc	<u>ent Loss</u>	in Weight of	Iron Wire	in Three	Months
C	orrosion	Environment		cteria Free	With Bacteria
	Ехр	eriment A			
Nutrient sea	water so	sturated with	nitr∋gen	1.2%	5.7%
Nutrient sea	water sa	aturated with	nitrogen	1.7%	10.0%
	Expe	eriment B			
Nutrient sea	water sa	sturated with	nitrogen	1.4%	11.0%
Nutrient sea	water s	iturated with	nitrogen	1.3%	10.2%

The Influence of Hyrdogen Sulfide on Corrosion. Bacteria were not essential for rapid corrosion in an anaerobic environment for their metabolic by-product, hydrogen sulfide, caused rapid and severa corrosion in an anaerobic environment in which no microorganisms were present (Table III). When hydrogen sulfide-producing bacteria were also present, corrosion occurred at an even greater rate.

Table III. Influence of Hydrogen Sulfide on the Anaerobic Corrosion of Iron Wire Immersed in Nutrient Sea Water

Percent Loss in Weight of Iron Wire in Three Months Mitrogen and Nitrogen Hydrogen Corrosion Environment Only* Sulfide Experiment A 1.2% 24.0% Bacteria-free nutrient sea water 1.7% 22.9% Bacteria-free nutrient sea water Experiment B Bacteria-free nutrient sea water 1.4% 14.7% Bacteria-free nutrient sea water 1.3% 14.8% Experiment A Nutrient sea water inoculated with bacteria 5.7% 52.6% 59.7% Nutrient sea water inoculated with bacteria 10.0% Experiment B Nutrient sea water inoculated with bacteria 11.0% 31.5% Nutrient sea water inoculated with bacteria 10.2% 35.6%

^{*}Same data as Table II

The Influence of Wood on Corrosion. In tropical areas, corrugated steel buildings corrode rapidly, especially at spots where the sheets of corrugated steel come into contact with a wooden frame. Two experiments were performed to see if wood has either a direct influence on the corrosion of iron immersed in demonized water or in sea water containing no other organic material, or an indirect influence through its ability to support the growth of bacteria that accelerate corrosion (Tables IV and V). No experimental evidence was obtained to indicate that wood exerts such an influence on corrosion though the results do not rule out the possibility that wood-decaying fungi in a terrestrial environment might produce organic acids that accelerate corrosion rates.

Table IV. Influence of Mixed Strains of Microorganisms on the Corrosion of Iron Wire in Contact With Wood and Immersed in Air-Saturated Water

wood and immersed	N 3		
Corrosion Environment	Exposure Time (Months)		Weight (%) Bacteria Present
Wire samples immersed in de-ionized water and covered with pine sawdust	2 2 4 4 4	9.2 9.3 16.5 15.1 17.8 22.5	5.2 8.1 17.1 18.8 22.0 16.2
Wire samples immersed in sea water and covered with pine sawdust	2 2 4 4 4	11.9 12.6 21.5 30.7 24.9 31.5	11.6 12.1 28.6 27.2 23.8 34.3

Table V. Influence of Wood on the Corrosion of Iron Wire Immersed in Sea Water

Percent Loss in Weight of Iron Wire in Three Months

Percent Loss in Weight of Iron W	1110 111 11111	e morrars
Corrosion Environment	No Sawdust* (%)	Sawdust Added (%)
Saturated with Air (Aerobic)		
Bacteria-free sea water .	12.5 10.1	8.1 10.9
Sea water inoculated with bacteria	12.1 6.3	8.8 14.8
Saturated with Nitrogen (Anaerobi	c)	
Bacteria-free sea water	1.7 2.0	1.3 1.3
Sea water inoculated with bacteria	1.7	0.9 0.9

^{*}Same data as Table I

Influence of Carbon Dioxide on Corrosion. Carbon dioxide is known to accelerate the corrosion of steel boilers and accordingly carbon dioxide as well as oxygen is commonly removed from feed water for boilers. The influence of carbon dioxide on corrosion is presumed to result from its effect on pH.

An experiment was performed to ascertain if carbon dioxide might participate in the corrosion process in a manner more fundamental than alteration pH (Table VI), but no evidence was obtained to indicate that such is the case. Corrosion rates in water aerated with carbon dioxide-deficient air were indistinguishable from corrosion rates in water aerated with normal air containing about 0.02 percent carbon dioxide. Only when carbon dioxide was present in concentrations sufficient to measurably influence pH, did it influence corrosion rates; and then its influence on corrosion was only slight.

Table VI. The Influence of Carbon Dioxide on the Corrosion of Iron Wire Immersed in Various Aqueous Solutions

Corrosion Environment	Initial	Final	Loss in W	leight of e_Months	
	pН	рH	CO ₂ ~rich Air		
De-ionized water		7.4-8.0 7.4-8.0	12.0	8,2 10.3	7.3 10.4
Sea water	_	6.7-7.4 6.7-7.4	11.6	7.2 7.9	8.6 7.5
Potassium-acid-phthalate buffer		5.7 - 5.8 5.7 - 5.8	43.3 47.5	39,5 42.6	43,2 47,6

Influence of Biochemicals on Corrosion. Tables VII-XII present data concerning the influence of various compounds of biochemical significance, most of them organic compounds, on corrosion rates. In the experiments summarized in Tables VII and VIII, the water was autoclaved and no inoculum was added. Nevertheless, the flasks were not bacteria-free as aseptic techniques were not employed for adding the test compounds. For those experiments summarized in Tables IX and X, aseptic techniques were employed throughout. Of the compounds tested, only acetazolamide had a pronounced and reproducible influence on corrosion rates (Table XI).

Acetazolamide was not as effective an inhibitor of corrosion as was the well-known corrosion inhibitor, sodium dichromate, which was included for comparison (Table X). Acetazolamide was decidedly more effective than was 2-mercaptobenzothiazole, a corrosion inhibitor frequently used in brine lines in the oil fields. Acetazolamide did not, however, retard hydrogen sulfide corrosion though it slightly inhibited growth of hydrogen sulfide-producing bacteria (Table XII)

Ascorbic acid (Table IX) stopped all corrosion for the first two weeks of the experiment. No doubt it did this by virtue of its strong reducing properties. Ascorbic acid is, however, gradually oxidized by air and by the end of the experiment, corrosion proceeded rapidly in the flask to which ascorbic acid had been added.

Table VII. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in De-ionized Water

Compound (All at conc. of 0.1 gms/100 ml.)		Loss in Weight of Iron Wire in Three Months (%)
Control (no additive)		16.1 22.0
Sodium sulfathia- zole	A bacteriostatic agent - one of the sulfa drugs. An inhibitor of the enzyme, carbonic anhydrase.	16.4 14.7
Ferric chloride	An end-product of the corrosion of iron in chloride solutions. An analytical agent for dissolving iron.	21.7
Kojic acid	A fermentation product produce from carbohydrates by a variet of microorganisms.	
Citric acid	A common intermediate of carbo hydrate metabolism of plants, animals, and microorganisms.	10.6 11.5
Hemin	Iron-containing pigment of hemoglobin, the oxygen-carrying protein of red blood cells.	19.0 17.1
Glycerin	A common product of bacterial metabolism; also a break-down product of fats and oils.	18.2 20.4
Car unic anhydrase	Respiratory enzyme catalyzing the reaction of carbon dioxide with water.	

Table VIII. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in Sea Water

Compound (All at conc. of 0.1 gms/100 ml.)	Description of Compound	Loss in Weight of Iron Wire in Three Months (%)
Control (sea water only)		15.5 16.9
Sodium sulfathia- zole	A bacteriostatic agent of the sulfa drug class. A weak in- hibitor of the enzyme, carbon- ic anhydrase.	18.0
Ferric chloride	An end-product of the corrosion of iron in chloride solutions. An analytical agent for dissolving iron.	19.0 20.7
Kojic acid	A fermentation product produced from carbohydrates by a variety of microorganisms.	16.4 15.1
Acetazolamide	A potent inhibitor of the respiratory enzyme, carbonic anhydrase.	3.4 1.3
Citric acid	A common intermediate of carbohydrate metabolism of plants, animals, and micro-organisms.	12.9 14.7
Hemin	Iron-containing pigment of hemoglobin, the oxygen-carrying protein of red blood cells	15.1 13.4
Glycerin	A common product of bacterial metabolism; also a break-down product of fats and oils.	15.7 15.8
Carbonic anhydrase	Respiratory enzyme catalyzing the reaction of carbon dioxide with water.	

Table IX. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in Bacteria-free Sea Water

Compound (All at conc. of 0.1 gms/100 ml.)		Loss in Weight of Iron Wire in Three Months (%)
Control (sea water only)		13.2 17.1
Pentanedione (acetylacetonate)	An organic compound related structurally to two fermenta-tation products. Complexes with iron salts.	24.1 20.5
Sodium sulfathia- zole	A bacteriostatic agent, one of the sulfa drugs; and an inhibitor of the enzyme, carbonic anhydrase	
Ferric chloride	An end product of the corrosion of iron in chloride solutions. An analytical agent for dissolving iron.	18.4 18.8
Kojic acid	A fermentation product produced from carbohydrates by a variety of microorganisms.	14.4 14.8
Acetazolamide	A potent inhibitor of the respiratory enzyme, carbonic anhydrase.	- 3.4 2.1
Citric acid	A common intermediate of carbo- hydrate metabolism of plants, animals, and microorganisms.	19.6 18.9
Hemin	Iron-containing pigment of hemo- globin, the oxygen-carrying protein of red blood cells.	14.9 15.9
Glycerin	A common product of bacterial metabolism; also a breakdown product of fats and oils.	15.7 17.6
Oxalic acid	A fermentation product. Is re- leased during decomposition of wood. Complexes with iron salts.	32.0 19.2

Table X. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in Bacteria-free Sea Water

		Loss in
Compound		Weight of Iron
(All at conc. of		Wire in Three
0.1 gms/100 ml.)	Description of Compound	Months (%)
Control		15.2
		14.1
(sea water only)		14.1
	Fermentation product with bread-	17.5
ol (or acetoin)	like odor. Its production by	16.3
	bucteria is used as basis for	
	classification.	
Citric acid	A common intermediate of carbo-	7.9
01110	hydrate metabolism of plants.	9.2
	animals, and microorganisms.	7.2
Tartaric acid	Fermentation product produced in	7.8
	wine making. Used to flavor soft	6.9
	drinks. Rotates polarized light.	
Indole	Produced by colon bacteria. Has	12.7
	distinct feces-like odor.	15.6
Benzoic acid	Produced by fruits and berries.	14.0
	is used as food preservative and	14.7
	as a rust inhibitor.	
Ascorbic acid	Used as a food supplement and as	9.3
(or Vitamin C)	an anti-oxidant to prevent ranci-	
	dity of rats and browning of	
	uppies	
Riboflavin	Vallow remant meadured by seems	
_	Yellow proment produced by micro-	
(or Vitamin B ₂)	organisms and used by all animals	5 • L" - t
	Participates in enzymic oxida- (
Thiamine	Distributed widely in nature.	1 2.5
(or Vitamin B.)	Produced by yeasts. Porticipates	
	in enzymic carboxylation reactions.	
		

Continued

Table X. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in Bacteria-free Sea Water (Contd)

Compound (All at conc. of 0.1 gms/100 ml.)	Description of Compound	Loss in Weight of Iron Wire in Three Months (%)
Sodium cyanide	Violent poison. A reducing agent which immobilizes hemoglobin. Complexes with iron compounds.	13.5 13.0
Sodium azide	A specific enzyme inhibitor. Blocks enzymatic oxidation and reduction but has no effect on glycolysis.	12.1 12.3
Sodium dichromate	A powerful oxidizing agent that inhibits the corrosion of iron immersed in sea water.	0.0 1.0
Allantoin	Birds excrete most of their protein nitrogen as wric acid which is oxidized to allantoin by bacteria.	18.1 16.3
2-Propylthioracil	An anti-thyroid agent.	15.9 15.4
Sulfaguanidine	A bacteriostatic agent - one of the sulfa drugs. Is an inhibitor of the enzyme carbonic anhydrase.	12.1 11.9
Sulfanilamide	A bacteriostatic agent - one of the sulfa drugs. Is an inhibitor of the enzyme carbonic anhydrase.	12.e 11.1
Cupferon	An organic compound that forms stable complexes with various iron salts.	23.2 22.4
Sodium barbital	A sedative with a line duration of action, iffects respiratory rate.	17.1 15.3

Continued

Table X. The Influence of Numerous Compounds of Biochemical Significance on the Aerobic Corrosion of Iron Wire Immersed in Bacteria-free Sea Water (Contd)

Compound (All at conc. of O.l gms/100 ml.)	Description of Compound	Loss in Weight of Iron Wire in Three Months (%)
Acetazolamide	A potent inhibitor of the respiratory enzyme carbonic anhydrase	2.2
2-Mercaptobenzo- thiazole	A rust inhibitor commonly used in the oil fields. Is also bacteriacidal to some organisms.	8.61 0.01
Kojic acid	Formentation product produced tom carbohydrates by a variety of micro-organisms. Reacts with iron salts.	11.0 20.3
Commerciai "pickling" agent	A mixture of compounds used to prevent the reaction of acid with iron during cleaning.	18 1 1 4.9

Table XI. Review of the Inhibiting Effect of Acetazolamide on Aerobic Corrosion in Sea Water

Carrosian Environment	Loss in Weight of Iron Wire in Three Months 5:1 Without With Acetazolam.de Acetazolam.de	
<u>Experiment A</u> Aire immersed in sea water	15.5 1€.€	4.4
Experiment E Wire immersed in backer; a-free sea water	13.7 (**)	3.4
<u>Experiment C</u> Asine (minersed in halterla-ties weaker		• •

"Same data as on Tables | VIII. IV. and to

Table XII. Influence of Acetazolamide on Anaerobic Sulfide Corrosion

	Loss in Weight of Iron Wire in Three Months (%)	
Corrosion Environment	Without Acetazolamide	With * Acetazolamide (0.1 gm/100 ml)
Aerated with Nitrogen Only (oxygen free)		
Bacteria-free nutrient sea water	1.4	1.4
Bacteria-inoculated nutrient sea water	11.9 10.2	1.4 7.5
Aerated with Mixture of Nitrogen and Hydrogen Sulfide (oxygen free)		
Bacteria-free nutrient sea water	14.7	15-6 15-3
Bacteria-inoculated nutrient sea water	31.5 35.¢	201 5 2013

^{*}Same data as on Table III

FINDINGS

Findings of Survey of Corrosion Problems at Naval Shore Facilities.

- l. The corrosion of buried tanks and pipelines is no longer as serious a problem at Naval activities as it was formerly. The problem is being solved by the construction of better drainage trenches, by the application of cathodic protection, and by the use of plastic pipelines.
- 2. Methods of preventing the corrosion of above ground metal structures are not as effective as is desired, but corrosion of such structures at Naval activities is a relatively minor problem.
- 3. The corrosion of major waterfront structures is the most serious problem associated with the deterioration of iron and steel structures at Naval activities. Corrosion of steel waterfront structures is most severe in the regions wetted periodically by sea water.

Findings of Review of Literature on Organisms that Influence Corrosion

- 1. Specific microorganisms can significantly accelerate corrosion by producing acids or by producing hydrogen sulfide, both of which are extremely corrosive to iron, steel, and certain other metals.
- 2. Accumulation of non-specific microorganisms and larger fouling organisms can foster the establishment of regions of differential oxygen concentrations on a metal surface. This condition leads to localized corrosion and pitting of the metal at the regions of lowest oxygen concentration
- 3. Microorganisms can reduce the general concentration of oxygen in the neighborhood of a metal surface or object and thereby retard its corrosion.

Findings of Experiments Performed at NCEL

- 1. In bacteria-free sea water, iron corrodes at least five times more rapidly in the presence than in the absence of oxygen.
- 2. When exposed to air, iron corrodes just as rapidly in bacteria-free sea water as in sea water containing numerous wild strains of fouling microorganisms.

- 3. Iron submerged in sea water from which oxygen is excluded rusts very slowly unless sulfate-reducing bacteria or their metabolic by-product, hydrogen sulfide, are present. To induce rapid anaerobic corrosion, the bacteria must be supplied with carbohydrates or other nutrients.
- 4. Most organic compounds appear to have but little, if any, influence on the corrosion of iron immersed in sea water unless the compounds are oxidizing or reducing agents or unless they significantly change the pH of the sea water.
- 5. The carbonic anhydrase inhibitor, acetazolamide, however, is an effective inhibitor of sea water corrosion and might be useful as an agent for imparting corrosion resistance to protective coatings and concrete.

CONCLUSIONS

Microorganisms frequently play a significant role in the corrosion of buried pipes and tanks, a problem which at Naval activities is frequently severe below the water line. Underground corrosion can all but be eliminated, however, by the application of cathodic protection, by the use of substitute materials, and by the construction of better drainage trenches. Bacterial processes probably do not significantly alter the aerobic corrosion of structures above ground, in any event a relatively minor problem at Naval activities.

Bacterial processes undoubtedly have a marked influence on the corrosion of structures wholly submerged in the ocean. In most instances the bacteria probably retard corrosion by reducing the concentration of oxygen, but in some instances bacterial processes promote very severe and rapid corrosion of iron submerged in the ocean.

Bacteria are of dubious significance in promoting corrosion in the splash zone, the area of most concern to the Navy. Sulfur-oxidizing bacteria and unicellular photosynthetic algae might accelerate splash zone corrosion, but even if economical methods were available to stop the growth of microorganisms on metal surfaces, splash zone corrosion would still proceed quite rapidly.

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Appendix A

BIBLIOGRAPHY ON BIOLOGICAL CORROSION

EXPLANATORY REMARKS

This bibliography includes many articles that do not pertain directly to biological corrosion. For example, a number of the listed articles pertain only to the physiology and distribution of sulfate-reducing bacteria, iron bacteria, or marine fouling organisms. Even though such articles may contain no reference to the corrosion of metals, they may be of considerable interest to one studying biological corrosion, and therefore they have been included in this bibliography. Similarly, a number of articles listed in the bibliography pertain more specifically to the deterioration of hydrocarbon fuels than to corrosion. A few such articles have been included because of the frequent association of the deterioration of metal fuel tanks and the deterioration of hydrocarbon fuels. Although the Bibliography on Biological Corrosion does not include abstracts of the referenced articles, in most cases it gives the location of readily available abstracts.

Location of Chemical Abstracts references are given by volume, column, and line; e. g., CA 44:ll67g, refers to Chemical Abstracts, Volume 44, Column 1167, Line g. The Chemical Abstracts are among the best known and readily available abstracts of scientific articles. Chemical Abstracts coverage of journals devoted to theoretical and fundamental studies is especially good, but its coverage of journals and technical magazines devoted to applied science and its coverage of government reports is incomplete.

The National Association of Corrosion Engineers (NACE) has for many years prepared abstracts from the technical literature of articles pertaining to corrosion. Their coverage of government reports and applied technical articles is especially good. Prior to 1962 the NACE Abstracts were printed on numbered punched cards which could be readily key-sorted into numerous sub-topics. Although NACE Cards are available in only a restricted number of libraries, the NACE Card numbers are given in the NCEL Bibliography on Biological Corrosion.

In 1962, NACE discontinued its printing of abstracts on punched cards and commenced publication of Corrosion Abstracts, a periodical. References to Corrosion Abstracts are given by volume, date, and page.

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In 1963 the Prevention of Deterioration Center (PDC) of the National Research Council prepared a Bibliography on Microbial Corrosion of Metals. The bibliography is readily available. It includes abstracts of articles on microbial corrosion, but it contains no index. References to the Prevention of Deterioration Center's Bibliography on Microbial Corrosion of Metals are abbreviated PDC Bi followed by the special number, usually a PDL-number, assigned to the article by the Prevention of Deterioration Center, and by the page number. A few articles abstracted by the Prevention of Deterioration Center and assigned a PDL-number were not included in their Bibliography on Microbial Corrosion of Metals. These are merely referred to by PDL-number.

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